

Phosphazene-cored star polymer bearing redox-active side groups as a cathode-active material in Li-ion batteries



Muhammet Aydin^{a,b}, Mesut Gorur^{c,*}, Faruk Yilmaz^{a,*}

^a Department of Chemistry, Gebze Technical University, Kocaeli 41400, Turkey

^b Central Research Laboratory, Namik Kemal University, Tekirdag 59030, Turkey

^c Department of Chemistry, Istanbul Medeniyet University, Istanbul 34700, Turkey

ARTICLE INFO

Article history:

Received 31 October 2015

Received in revised form 17 February 2016

Accepted 18 February 2016

Available online 23 February 2016

Keywords:

Organic radical battery

Nitroxyl stable free radical

Atom transfer radical polymerization

Star polymer

Redox-active polymer

ABSTRACT

A new hexa-armed star polymer bearing 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-pending polymer chains emanating from a phosphazene core (**P2**) was prepared and used as the cathode material in Li-ion battery assembly. The properties of the assembled battery (**BP2**) were compared with those of **BL2** assembled using its linear counterpart (**L2**). Their spin concentrations investigated via solution electron spin resonance (ESR) measurements were found to be almost the same. The charge/discharge capacities and energy densities of **BP2** were considerably higher than those of **BL2**. However, they exhibited comparable charge/discharge efficiencies and their discharge capacities dropped to similar percentages of their initial values.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Commercialization of new portable electronic devices (e.g., computer, cell phone, and consumer electronics) and electricity-powered vehicles urged scientists to develop rechargeable batteries with improved properties. These batteries are expected to be fast-charging, lightweight, small, thin, environmentally safe, and capable of providing high power and energy capacities [1]. The commonly used rechargeable batteries, such as nickel–cadmium (NiCd), nickel–metal hydride (NiMH), lithium-ion containing cobalt oxide (LCO) and manganese oxide (LMO), and nickel–manganese–cobalt oxide (LNMCO), mainly depend on inorganic rare earth materials [2]. Besides, these battery systems have some limitations, such as self-discharge upon long-term storage, low power density, memory effect, and energy and manufacturing costs [3]. In addition, these batteries are regarded as environmentally unsafe as they contain hazardous materials [4].

Application of rechargeable batteries based on organic electrode-active materials began in the early 1980s. In the early months of 1981, Shirakawa, McDiarmid, and Heeger, by extending their work on electrical conductivity of polyacetylene, reported that p- and n-doped polyacetylene can be used in rechargeable organic batteries [5]. Then, the feasibility of employing other electrically conductive polymers, such as polyaniline (PA), polythiophene (PThi), polypyrrole (PPy), and

their derivatives, was investigated in terms of their reversible doping behaviors. These conductive polymers were found to have low redox capacities because of their insufficient doping level (~10%), which limited their application in rechargeable batteries. Moreover, chemical instabilities of their doped states caused their self-discharge and reduction in charging capacities [6]. On the contrary, in the recent studies of PPy [7, 8] and PThi [9,10] as cathode materials in Li-ion batteries, promising results in terms of discharge capacity and cycling performance were reported, but their discharge plateau levels were ≤ 2 V and discharge voltage decreased continuously during the experiments. In addition to the conductive polymers, tetrathiafulvalene, carbazole, ferrocene, and stable organic radicals containing polymers were used in the preparation of cathode layers for Li-ion batteries [11–16].

Polymers with redox-active groups have attracted much attention in recent years, because of their potential applications in electrode-active materials for batteries. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), a nitroxyl radical, is one of the most important stable radicals, because of its high radical intensity per unit mass, high stability in redox reactions, and its ability to survive for a year in aprotic solvents containing 1 M LiPF₆ (electrolytic media) [17]. TEMPO radical containing poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) polymer was first employed as a cathode-active material in a rechargeable lithium battery by Nakahara et al. in 2002 [18]. The result of the research on organic radical materials demonstrated that these materials offered many advantages over metal-based ones. The theoretical discharge capacity of PTMA is 112 mAh/g [19], which is comparable to that of LiCoO₂ (140 mAh/g) [20]. The TEMPO radical has two redox

* Corresponding authors.

E-mail addresses: mesut.gorur@medeniyet.edu.tr (M. Gorur), fyilmaz@gtu.edu.tr (F. Yilmaz).

pairs: through one-electron oxidation to oxyammonium cation and one-electron reduction to aminoxy anion. Therefore, TEMPO-bearing polymers can be employed as both cathode- (p-type) and anode-active (n-type) materials. Suga et al. prepared a totally organic radical battery, in which poly(galvinoxystyrene) with phenoxy radical groups and TEMPO side-functional polynorbornene were used as anode- and cathode-active materials, respectively [21]. Koshika et al. reported that poly(TEMPO vinyl ether) (PTVE) cathode material demonstrated ultra-fast and quantitative full charging even at 1200 C, retaining 97% (127 mAh/g) of its calculated capacity [22]. Suga et al. synthesized poly(nitroxystyrene)s with different substituents and stated that their redox properties can be tuned by the electronic effects of substituent groups for application as p- and n-type electrode materials in all-organic radical batteries [23].

To date, several methods have been proposed for the synthesis of TEMPO-bearing polymers. Production of PTMA by anionic [24,25] and group transfer polymerizations [26] of TEMPO methacrylate monomer has been reported in the literature. In addition, cationic polymerization of TEMPO-containing vinyl ether monomer was demonstrated by Suguro et al. Cationic and anionic polymerization methods require stringent reaction conditions, whereas group transfer polymerization technique suffers from high polydispersity index (PDI) values [27]. On the contrary, radical polymerization methods require protection of nitroxyl unit. Therefore, first, the amine-bearing precursor (2,2,6,6-tetramethylpiperidin-4-yl methacrylate (TMPM)) is polymerized and then piperidine groups of the resulting polymer are oxidized using appropriate oxidizing agents, yielding TEMPO-containing targeted polymer. Free-radical polymerization is the most straightforward radical polymerization method; however, it suffers from poor control over molecular weights and PDI values of the yielded polymers [18,27–30]. Nitroxide-mediated polymerization (NMP), which is widely used for the controlled radical polymerization of styrenic monomers [31], is not a convenient method to obtain well-defined polymers from methacrylate-based monomers [32]. On the other hand, reversible addition-fragmentation chain transfer (RAFT) polymerization has some drawbacks resulting from the interactions of the secondary amine of piperidine group with the thiocarbonylthio group of the chain transfer agent [33,34]. In the atom transfer radical polymerization (ATRP) method, the free secondary amine of the TMPM monomer may interfere with the catalyst through interactions with the copper salt, which may lead to termination reactions [35]. Hauffman et al. showed that well-defined PTMA polymers can be obtained via ATRP method by optimizing reaction parameters [36]. In this method, careful optimization of the parameters, such as catalyst system, solvent type (or bulk in some cases), temperature, and initiator functionalities, is important to produce well-defined polymers with narrow molecular weight distribution [37,38]. Furthermore, ATRP is a very convenient method to synthesize tailor-made star polymers [39,40] and decorate the surfaces of insoluble substrates with polymer brushes [41–43]. Ernould et al. grew poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMPM) via ATRP of TMPM monomer and oxidized the piperidine side units of PTMPM arms to yield electrochemically active nitroxide-bearing PTMA polymer brushes on multiwalled carbon nanotubes (MWCNTs) [44]. The obtained PTMA-grafted MWCNTs were used as cathode-active materials in organic radical batteries. Lin et al. prepared silica nanoparticles with PTMA brushes via ATRP of TMPM monomer using bromide-functional silica initiators and subsequent oxidation of obtained PTMPM polymer arms [45]. Wang et al. prepared PTMA brushes grafted on indium tin oxide (ITO)-coated glass or poly(ethylene terephthalate) (PET) surfaces and used them as thin-film cathodes in organic radical batteries [46].

The synthesis of macromolecules with well-defined molecular architectures and compositions has been the pursuit of polymer scientists for many years. Star-shaped polymers have attracted the attention of scientists because of their possible processing advantages resulting from their compact structure and higher degree of end-group functionality

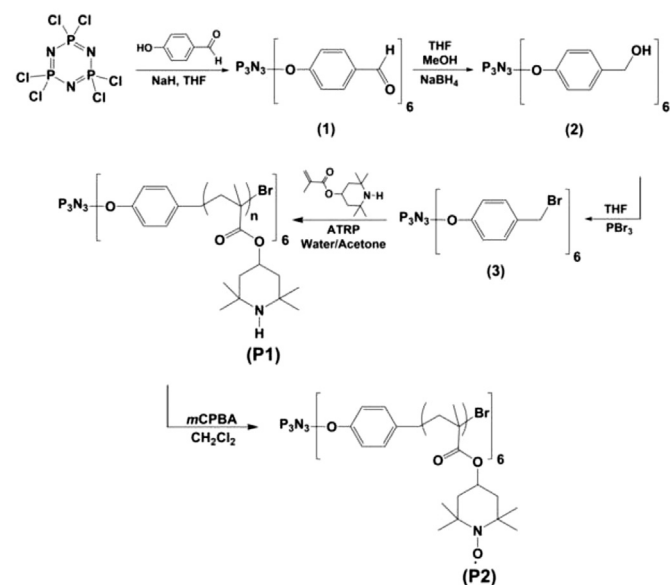
[47,48]. They have been used in a variety of applications, including modifiers for thermoset resins [49,50], photodynamic therapy [51], drug delivery [52–55], gene delivery [56], encapsulation of nanomaterials [57, 58], catalysis [59], selective cation separation [60,61], scaffolds for tissue engineering [62], and protein separation via capillary electrophoresis [63]. Star-shaped polymers can be prepared via mainly two synthetic approaches: (1) the core-first method (divergent), in which polymer arms are emanated from initiating sites of a multifunctional initiator compound [64] and (2) the arm-first method, in which pre-synthesized polymer arms, having proper functional units, couple with a core molecule [65]. In this context, several cyclic phosphazene derivatives with proper functional groups have been used as multifunctional initiators to synthesize star-shaped polymers via core-first approach [64,66–68].

In this study, a new hexa-armed PTMA star polymer (**P2**) with a phosphazene core and nitroxyl stable free radical (TEMPO) side groups was synthesized for investigating the effect of star-shaped topology on the characteristics of Li-ion batteries. The rates of redox reactions taking place during the operation of battery depend on the counter-ion diffusion characteristics [69]. It is well known that star polymers have less chain entanglement than their linear counterparts, and they may enhance the counter-ion diffusion characteristics. To the best of the authors' knowledge, this is the first study of its kind to use a star-shaped polymer as cathode-active material for Li-ion battery application. For this purpose, first, a phosphazene compound containing six bromide functional groups was prepared through a series of chemical reactions starting from hexachlorocyclotriphosphazatriene and used as the multi-site initiator in the ATRP of TMPM monomer, yielding a hexa-armed PTMPM star polymer (**P1**). Finally, piperidine units of **P1** were oxidized to produce **P2** with redox-active TEMPO side units (Scheme 1). **P2** was then employed as the cathode-active material in the preparation of rechargeable Li-ion coin cell. A linear PTMA polymer was also prepared to compare its battery characteristics with those of the star-shaped PTMA polymer (**P2**).

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$, Alfa Aesar, 98%) was purified by crystallization from dry hexane. Sodium hydride (NaH, Merck,



Scheme 1. Synthetic pathway of star-shaped hexa-armed PTMA polymer with nitroxyl side groups (**P2**).

Download English Version:

<https://daneshyari.com/en/article/5209499>

Download Persian Version:

<https://daneshyari.com/article/5209499>

[Daneshyari.com](https://daneshyari.com)